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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C03C 13/06, 3/087, 3/089		A1	(11) International Publication Number: WO 96/01793 (43) International Publication Date: 25 January 1996 (25.01.96)
(21) International Application Number: PCT/SE95/00714		(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG).	
(22) International Filing Date: 13 June 1995 (13.06.95)			
(30) Priority Data: 9402405-6 7 July 1994 (07.07.94) SE			
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<p>(54) Title: COMPOSITION OF MATERIAL</p> <p>(57) Abstract</p> <p>The invention relates to glass compositions for the manufacture of mineral wool having favourable physiologic properties as well as good production technical, production economical and product favourable properties. The glass composition contains SiO_2 in the amount of 45-55 % by weight, Al_2O_3 in the amount of 0-8 % by weight, B_2O_3 in the amount of 0.3-5 % by weight, Fe-oxides in the amount of 0-10 % by weight, alkalic earth oxides in the amount of 32-45 % by weight and alkalic oxides in the amount of 0-6 % by weight. Also favourable relationships of different oxides are defined.</p>			

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COMPOSITION OF MATERIAL

Suspicions have been directed on mineral wool from medical professional viewpoints depending on misleading parallels to asbestos. In front of all the risque of lung cancer has been discussed. In spite of intensive epidemiological

5 investigations no connections have been verified, however, between working with mineral wool and lung cancer or any other disease. Also not inhalation tests, in which test animals have inhaled large amounts of mineral wool fibres, have lead to any increased origin of cancer. These results concern available and commercial fibres, and it is not clear to what extent said results can be applied

10 also to other types of fibres. Possibly there is a need for further investigations.

It is, however, very expensive to perform epidemiological studies and inhalation studies, and such studies take long time to perform, generally several years. Epidemiology also is relatively insensitive. Therefore attempts have been

15 made to find a method for screening, meaning to find a method for identifying types, in the present case types of mineral wool fibres which may cause a risque of origin of diseases. Cases thus identified can later be subjected to more expressivly stating tests for determining whether or not there is such actual risque. Another aspect is that fibre types which give results for a correctly

performed screening test should be considered free from diseases risques.

20 Screening tests may be IP tests, intraperitoneal or intrapleural introduction, that is introduction of fibres in the abdominal cavity and in the pleura of test animals. Such tests are considered having a high sensitivity with a low amount of false negative results, meaning cases in which a material which may cause a disease risques actually happen to be considered free in the test.

25 There may, on the contrary, be a high amount of false positive results. The knowledge thereof is, at present, too low.

Also IP tests can be expensive and take several months to perform. It is also un-ethical to un-necessarily use test animals for such purposes. Therefor in-vitro methods have been tested, which methods can me performed with a

30 reasonable equipment and in a time of only a few days. Such methods are of two categories, biochemical and chemical methods.

In biochemical methods the fibres are brought into contact with live cells or cell materials, and the biochemical reactions are investigated, for instance the formation of free radicals.

35 The chemical methods are often based on the phenomena that mineral

wool fibres can be solved in polar liquids, for instance simulated body liquids. There are reasons to believe that fibres which are quickly solved or fragmentated to very short pieces represent a low risque, or no risque at all.

It has been suggested that a chemical screening be performed prior to the

- 5 IP test, thereby hopefully drastically reducing the number of types of fibre which have to be IP tested. It has thereby been meant to create an index built on the composition of the glass of the fibres and by means thereof to divide the glass compositions into three groups: a first group which probably may get free in an IP test, that is a group which gives a negative outcome; a second group for which 10 there is reason to believe that the glass composition could not get free in an IP test; and a third category which is a group for which nothing can be determined with reasonable likelihood by means of the index and which therefore has to be subjected to IP tests.

An index according to this thought is Wardenbach index, WI, which is

- 15 calculated by the formula (the amounts in % by weight):

$$WI = BaO + CaO + MgO + Na_2O + K_2O + B_2O_3 - 2 \cdot Al_2O_3.$$

The creators of this index believe that fibres having the diameter $< 3\mu m$ and a length of more than three times the diameter will probably not get free in a standardised IP test if WI is less than 25, whereas it is the opposite if WI is 20 greater, or equal to 40. In the interval $25 < WI < 40$ certain other estimations have to be used.

The Wardenbach index seems to be an empirical construction which points to a glass having a certain instability which could cause the actually sought high solubility, that is a short lifetime for the fibres of the organism.

- 25 The solubility is not, however, the only determining property of a fibre. Other properties are its morphology and the ease by which the fibre is broken into fragments. There is also nothing of said index which indicates the technical usefulness of the glass, for instance its capability of becoming melted, of becoming fibrillated or other properties of the fibres manufactured from the glass 30 in question.

The solubility of a fibre is separately a complicated phenomena. Several studies have been performed in the area, for instance by Scholze and Conradt "An in-vitro study of the chemical durability of siliceous fibres", Ann occup. Hyg., Vol 31, No 48, pp 683-692, 1987. What has made the situation complicated is 35 that fibres may be attacked by the contacting liquid in at least four various ways.

A first way is by a homogenous solution, that is when ions from the glass of the fibres enter a solution by the same speed over the entire fibre surface without any noticeable change of the remaining glass. The second way is a selective dissolving, whereby certain ions enter a solution more easily than other ions.

5 This means that the remaining glass is impoverished of said dissolved ions. Both said ways make the diameter of the fibres become reduced by time but basically evenly over the entire length of the fibre.

A third way is to transfer the glass of the fibre to a gel down to a certain depth. The layer of gel is thereafter broken off and a new layer of gel is formed.

10 Also this method leads to a basically even reduction of the diameter of the entire length of the fibre.

The fourth way is to form cavities or scars at the surface layer of the fibre. The cavities can be relatively deep and said cavities may possibly be a part of the reason that the fibres are broken up into short pieces of the tissues. Said 15 phenomena has often been noted in animal tests. The shortening of the fibres makes it easy to move off the fibres. It is considered that fibres below a certain minimum length, which by various sources is mentioned as 5-20 μm , are not cancerogene.

In short this means that a fibre, the dimension of which might make a 20 cancer induction possible, may fall outside said dimensions in one or more ways. The study of said various mechanisms therefore is of importance in connection to the medical circumstances. Unfortunately there is no complete theory why different types of fibres act as differently as said above, and existing hypotheses are in part contradictory. One reason therefore is the experimental difficulties. It 25 is question of a process in microscopical scale in which the conditions are heterogene. The pH value is without doubt of great importance in these connections, and said pH value is not the same inside the cells as between the cells. It has been said that this difference can be one of the most important parameters as concerns the decomposition of the fibres.

30 Among the explanations of the differences between various fibres can be found differences in chemical composition, non-homogeneity of the chemical composition and micro tensions in the fibres depending thereon and depending on the ultra quick cooling that the glass is subjected to in connection to the fibrillation. Also impurities in the fibres, air blows and encased particles can be 35 explanations.

To a great extent the experiments have to be performed in-vitro, and this necessitates many compromises of model technical and observation technical character. Thus there is preferably used fibres having greater dimensions than for the inhalable fibres, there is not used physiological liquids but simulated such liquids, for instance Gamble's solution having or not having the organic components.

The observations can only in part be quantified, and the observations and the interpretations thereof are to a great extent subjective. Depending thereon it is not very easy to reproduce same.

10 The present invention is partly built on studies of fibres manufactured in model scale, wherein several kilos of a mineral batch is melted in an electrode furnace, whereupon the melted mineral is fibrillated by a so called cascade spinning machine in which the melted mineral is supplied to the envelope surface of a rapidly rotating steel cylinder, a spinning wheel, which is cooled at 15 the inner thereof, and from there the melted mineral is in part thrown out as fibres and is in part thrown onto the succeeding spinner wheel etc.

Certain studies have been carried out on sedimented fractions of thin fibres, other studies have been carried out on individual course fibres. The fibres have been exposed to different chemical environments and have been studied 20 by traditional chemical analysis, by means of scanning electronic microscope, SEM, for chemical analysis of small section and for observation of changes of the surface.

A technical glass, as will be found in mineral wool fibres, contains several main oxides which co-operate with each other in a complicated manner. The 25 principle role of some of said oxides is, indeed, known for certain composition areas but the details are mainly unknown as concerns the in the complex interaction. In a system having only three components, for instance the oxides Si, Al and Na it is possible to find an area in a three dimensional co-ordinate system represented by a volume, in which stable glass can be manufactured. It 30 is possible to thereafter identify various part volumes, regions, which have different properties. Stepwise transitions do not exist, but the regions have to be defined by means of one property, for instance the solubility measured by a particular method.

Within each region there should be at least one point, which, considering 35 the studied property, represents an extreme value, either a maximum or a

minimum value. Since such extreme curves many times have relatively level characteristics it can be difficult to define the exact extreme point.

Since technical glasses contain many more components than the above discussed three components there is, in practice, question of n-dimensional 5 volumes and regions in an n-dimensional system.

During the work, thus described, several regions have been found, for which there seems to be favourable properties, as seen from the possibility that fibres having such composition ought to give negative results in IP tests.

Such observations are not sufficient for finding out technically useful 10 compositions for mineral wool fibres. It is also necessary that the glass has a good meltability, that it allows a fibrillation with a good yield, and that the material also offers a good production economy and gives fibres and wool having suitable properties. Therefore also full scale tests have been made for manufacture and test of ready products.

15 Also such a judgement involves a number of subjective elements. After a large number of tests it has been possible to further define the regions which in the chemical evaluation were considered favourable, so that the invention relates to compositions which both act as desired in a bio-environment and are suitable for rational production of mineral wool having good properties for the product to be useful.

20 In practice it is rarely possible to vary one single oxide of the glass in relation to the other oxides, but generally there is, concurrently therewith, obtained variations in several of the oxides. This difficulty can be overcome by treating test data by means of statistical methods as a multiple factor analysis in 25 which the role of the individual oxides can be distinguished. In such analysis it is also possible to operate with variable transformations and with secondary variables which are functions of several primary variables.

30 In a complete analysis of the biologically interesting properties in-vitro, relevant production factors and the remaining properties of the fibres by means of a creative use of statistical methods the following composition areas have 35 been identified as highly valuable. The following table contains amounts in % by weight in three stages A, B and C. The table is to be understood so that, for a certain oxide, irrespective what values exist for the other oxides, the A-area is a minimum demand, the B-value is a better choice and the C-value is the best choice. If an amount of an oxide changes from having existed outside the B-area

to be present inside the B-area a noticeable improvement is obtained even if all the other oxides is present outside the B-area.

Oxide	A	B	C
SiO ₂	45 - 55	46 - 50	47 - 49
Al ₂ O ₃	≤ 8	≤ 6	≤ 4
B ₂ O ₃	0.3 - 5	0.5 - 5	1 - 4
FeO + Fe ₂ O ₃	≤ 10	≤ 8	≤ 6
CaO + MgO	32 - 45	35 - 42	36 - 40
Na ₂ O + K ₂ O	≤ 6	≤ 4	≤ 2

5 The meaning of the table thus is that, if for instance the content of Al₂O₃ is lowered from 5 to 3 by weight, there is obtained a noticeable improvement in the total evaluation of the usefulness of the glass. The content of B₂O₃ can preferably be rather low since an effect is obtained already at small amounts thereof. It is considered that at least 0.3 % by weight is needed.

10 The values of the table are in % by weight. The sum of ferric oxides is expressed as FeO, the sum of alkalic earth as CaO and the sum of alkalic oxides as Na₂O. In compositions of the described type there can also exist minor amounts of other oxides like oxides of Mn and Ti. Experiences show that amounts of 0.5 - 2 % by weight are suitable.

15 An addition of phosphorus has a favourable effect if added in an amount of between 1 and 4 % by weight.

20 Within the above mentioned frames it is possible to find compositions for which BaO + CaO + MgO + Na₂O + K₂O + B₂O₃ - 2 • Al₂O₃, all in % by weight, is greater than 30, even greater than 40. The invention explicitly includes such compositions.

25 The studies which have lead to the invention as presented above also showed that the relationship B₂O₃ / Al₂O₃, as calculated in % by weight, is of significant importance. The relationship preferably is greater than 0.2, preferably also greater than 0.4.

25 Also the relationship MgO / CaO is of importance.

The invention is otherwise defined by the claims.

The composition according to the invention lies, as concerns the content of SiO_2 , within the area in which there is traditionally found rockwool. Rockwool having an addition of boron is described in the Danish patent application No

5 8301226. Adding boron to a rockwool glass does not at all, however, lead to a useful glass, it is necessary to, concurrently therewith, reduce the amount of Al_2O_3 .

Glass compositions according to the invention are particularly adapted for melting in cupola furnaces or in electrode furnaces and a subsequent fibrillation

10 by means of a cascade spinning machine.

C L A I M S

1. The present invention relates to compositions of glass by means of which mineral wool is manufactured in that the glass in melted form is supplied to a fibrillation apparatus by means of which fibres are created, characterized in that the glass contains the following oxides, the amounts given in % by weight:

SiO_2	45 - 55
Al_2O_3	≤ 8
B_2O_3	0.3 - 5
$\text{FeO} + \text{Fe}_2\text{O}_3$	≤ 10
$\text{CaO} + \text{MgO}$	32 - 45
$\text{Na}_2\text{O} + \text{K}_2\text{O}$	≤ 6

in which the sum of ferric oxides is expressed as FeO , the sum of alkalic earth as CaO and the sum of alkalic oxides expressed as Na_2O .

10 2. Glass compositions according to claim 1, characterized in that the content of SiO_2 is at least 46 % by weight, preferably at least 47 % by weight.

3. Glass compositions according to claim 1 or 2, characterized in that the content of SiO_2 is at most 50 % by weight, preferably at most 49 % by weight.

15 4. Glass compositions according to any of the preceding claims, characterized in that the content of Al_2O_3 is at most 6 % by weight, preferably at most 4 % by weight.

5. Glass compositions according to any of the preceding claims, characterized in that the content of B_2O_3 is at least 0.5 % by weight, preferably 20 at least 1 % by weight.

6. Glass compositions according to any of the preceding claims, characterized in that the content of B_2O_3 is at most 5 % by weight, preferably at most 4 % by weight.

7. Glass compositions according to any of the preceding claims, 25 characterized in that the content of ferric oxides, calculated as FeO , is at most 8 % by weight, preferably at most 6 % by weight.

8. Glass compositions according to any of the preceding claims,

characterized in that the content of alkalic earth oxides, calculated as CaO, is at least 35 % by weight, preferably at least 36 % by weight.

9. Glass compositions according to any of the preceding claims,
characterized in that the content of alkalic earth oxides, calculated as CaO, is at most 42 % by weight, preferably at most 40 % by weight.

10. Glass compositions according to any of the preceding claims,
characterized in that the content of alkalic oxides, calculated as Na₂O, is at most 4 % by weight, preferably at most 2 % by weight.

11. Glass compositions according to any of the preceding claims,
10 characterized in that said compositions also contain 0.5 - 2 % by weight of manganese oxide.

12. Glass compositions according to any of the preceding claims,
characterized in that the compositions also contain 0.5 - 2 % by weight of titanium oxide.

15 13. Glass compositions according to any of the preceding claims,
characterized in that the compositions also contain 0.5 - 5 % by weight of P₂O₅.

14. Glass compositions according to any of the preceding claims,
characterized in that the compositions also contain at least 1 % by weight, preferably at least 3% by weight of ferric oxides, calculated as FeO.

20 15. Glass compositions according to any of the preceding claims,
characterized in that the amount of

CaO + MgO + Na₂O + K₂O + B₂O₃ - 2 • Al₂O₃,
all in % by weight, is at least 30, preferably at least 40.

16. Glass compositions according to any of the preceding claims,
25 characterized in that the relationship B₂O₃ / Al₂O₃, calculated in % by weight, is higher than 0.2, preferably also higher than 0.4.

17. Glass compositions according to any of the preceding claims,
characterized in that the relationship MgO / CaO, calculated in % by weight, is higher than 0.15, preferably also higher than 0.2.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE 95/00714

A. CLASSIFICATION OF SUBJECT MATTER		
<p>IPC6: C03C 13/06, C03C 3/087, C03C 3/089 According to International Patent Classification (IPC) or to both national classification and IPC</p>		
B. FIELDS SEARCHED		
<p>Minimum documentation searched (classification system followed by classification symbols)</p> <p>IPC6: C03C</p> <p>Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched</p> <p>SE,DK,FI,NO classes as above</p>		
<p>Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)</p>		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>WO 9002713 A1 (ROCKWOOL INTERNATIONAL A/S), 22 March 1990 (22.03.90), page 4, test 5</p> <p>---</p> <p>WO 9209536 A1 (PAROC OY AB), 11 June 1992 (11.06.92), page 6, ex.Ia - IIb</p> <p>---</p> <p>EP 0459897 A1 (ISOVER SAINT-GOBAIN), 4 December 1991 (04.12.91), page 5, table 1, ex 5, 6</p> <p>---</p> <p>-----</p>	1-17
A		1-17
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/SE 95/00714

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
WO-A1- 9002713	22/03/90	EP-A-	0454674	06/11/91
WO-A1- 9209536	11/06/92	AT-T- AU-A- DE-D,T- EP-A,B- SE-T3- FI-B-	117662 8908791 69107091 0558548 0558548 93346	15/02/95 25/06/92 17/08/95 08/09/93 15/12/94
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